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Large atomic displacements associated with the nitrogen antisite in GaN

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We present results of an extensive theoretical study of the nitrogen antisite in GaN. The neutral antisite in *c*-GaN is reported to exhibit metastable behavior similar to the arsenic antisite in GaAs. The feature of interest is the existence of the negative charge states of the nitrogen antisite. Their stability is a consequence of the large band gap. The nitrogen antisite undergoes in the negative charge states a large spontaneous Jahn-Teller displacement in the [111] direction, both in the cubic and in the wurtzite phase. The connection between the nitrogen antisite and the yellow luminescence commonly observed in GaN is discussed. [S0163-1829(96)05824-9]

GaN is a promising material for blue-emitting optical devices due to the direct wide (3.4 eV) band gap.[1,2] The high structural stability, a common property for all the III-V nitrides, is another advantage which favors applications in hostile environments. The recent development in GaN crystal growth techniques has led to a dramatic improvement in the quality of samples. The difficulty in obtaining *p*-type GaN has been overcome using Mg as the dopant.[3,4] Despite the progress in growth methods, several questions, mainly related to native defects or impurities, remain without a definite answer. Among these are the source of the *n*-type conductivity and the origin of the yellow luminescence, which are both typical for GaN crystals. The microscopic origin of the many deep levels in the GaN band gap has also remained unidentified. To summarize, the knowledge of electronic properties of defects in GaN is still far from the state achieved in, e.g., GaAs. In this paper we present the results of *ab initio* calculations of the nitrogen antisite (N_{Ga}) in GaN. The *neutral* antisite in *c*-GaN is shown to have metastable behavior which is in many respects similar to that of As_{Ga} in GaAs.[5,6] According to our calculations, the *negatively* charged N_{Ga} defects undergo spontaneously large atomic displacements from the ideal geometry, and the induced deep levels are well within the band gap. This is a phenomenon induced by the large value of the band gap in GaN; therefore it is not observable, e.g., in GaAs, but is likely to exist in other wide-band-gap III-V materials.

Our calculations are based on the density-functional theory (DFT) in the local-density approximation (LDA).[7] We have performed most of the calculations with both 32 and 54 atom supercells, and the consistency in the results indicates convergence with respect to system size. For the *k*-point sampling we use in both cases the $2\times2\times2$ Monkhorst-Pack mesh.[8] A plane-wave basis for the valence wave functions is used and the core electrons are replaced by pseudopotentials. For nitrogen we use the Vanderbilt ultrasoft pseudopotential[9] and for gallium a standard norm-conserving pseudopotential.[10] Ga *d* electrons are treated with the nonlinear core-valence exchange-correlation scheme (nlcv-xc).[11] The kinetic energy cutoff for the plane-wave basis is 25 Ry. Our tests indicate that the results presented are well converged already with a 20-Ry cutoff confirming the advantages of using the Vanderbilt-type pseudopotentials for the first row elements. For the electronic structure minimization we employ damped second-order dynamics,[12] which we find to be especially effective in the case of GaN. The calculations are performed in cubic (zinc-blende) GaN unless otherwise stated.

Chadi and Chang[5] and Dabrowski and Scheffler[6] proposed that the $EL2$ metastability in GaAs can be explained by the $As_{Ga} \rightleftharpoons V_{Ga} + As_i$ structural transition. Therefore it is natural to ask whether the same phenomenon exists for *neutral* N_{Ga} in GaN. In Fig. 1(a) we show that this is indeed the case. The horizontal axis describes the displacement of N_{Ga} from the substitutional site along the [111] direction. The curves correspond to total energy calculations where all other atoms except the N_{Ga} are kept at their ideal lattice sites. In this static calculation the local minimum associated with the displaced configuration is found to be approximately 1.0 eV higher in energy than the ideal antisite. The barrier separating these two atomic positions is estimated to be 1.4 eV. In the single particle picture the two excess electrons of the neutral anion antisite at the substitutional site occupy the antibonding deep level $1a$ in the gap (we follow here the notation by Dabrowski and Scheffler[6]). At the barrier a level crossing occurs and the $2a$ level becomes the lowest and doubly occupied.

The metastable behavior changes dramatically in GaN when atomic relaxations are allowed. The relaxation energy at the substitutional site (0.3 eV) is considerably smaller than at the displaced position (1.2 eV) and therefore the displaced site now becomes energetically nearly equal to the substitutional site. The relaxation at the displaced site conserves the C_{3v} symmetry and the three atoms, forming the ''base'' triangle of the nitrogen tetrahedron surrounding the displaced antisite atom, relax strongly inwards. The details of the atomic relaxation are given in Table I.

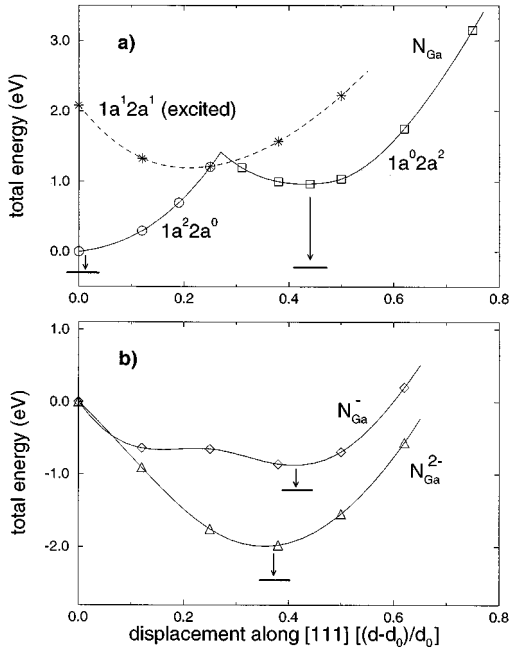

FIG. 1. The total energies for the (a) neutral and (b) negatively charged nitrogen antisites. The zero position denotes the ideal geometry and the displacement in the [111] direction is measured in units of the nearest-neighbor distance (d_0). Arrows and the corresponding horizontal lines refer to calculations where all the atoms are allowed to relax.

The mechanism leading to the $As_{Ga} \rightarrow V_{Ga} + As_i$ structural transition in GaAs, proposed by Dabrowski and Scheffler,[6] is optical absorption. We suggest that a similar mechanism should also be present in GaN. In Fig. 1(a) we show with the dashed line the total energy when the electronic system is in an excited state ($1a$ and $2a$ singly occupied). The Jahn-Teller effect causes the N_{Ga} in the excited state to spontaneously distort in the [111] direction, and by following the excited energy curve the probability for the barrier crossing is considerably enhanced. Although the calculation of such an excited state is not strictly valid in density-functional formalism, we believe that at least the qualitative trend is correct.

In Fig. 1(b) we present the total energy curves for the *negatively* charged antisites. The addition of an electron to the system leads to a spontaneous move of the antisite atom in the [111] direction, driven by the Jahn-Teller effect similar to the neutral excited case. This effect can be seen to be even more pronounced in the *doubly negative* charge state. When the charge state is raised to *triply negative* and the $1e$ level becomes singly occupied, the system distorts from the C_{3v} symmetry, again due to the Jahn-Teller effect. The antisite atom moves off from the [111] axis to a position where even the highest single particle level persists as a deep localized state in the gap. In Fig. 2 we have collected the single particle energies for the N_{Ga} in different charge states and atomic positions. At the displaced configuration all the occupied levels are well in the band gap, which is in striking contrast to GaAs where in the displaced configuration only the $1a$ state is within the band gap and the $2a$ and $1e$ levels move into the conduction band.[13] This observation is due to the large value of the band gap in GaN (Ref. 14), which allows the existence of many more deep electronic levels in the band gap than in narrow-bandgap semiconductor materials.

TABLE I. Details of the atomic relaxation with N_{Ga} in different charge states. d_1 denotes the bond length between the antisite atom and the nearest-neighbor nitrogen on the [111] axis. d_2, d_3, and d_4 give the distances to the remaining three nearest-neighbor nitrogen atoms, respectively. The values are in units of the nearest-neighbor distance of the perfect lattice. The measured change in volume $[\Delta V = (V - V_0)/V_0]$ is related to the tetrahedron formed by the four nitrogen atoms surrounding the antisite. Note that the values for d_2, d_3, and d_4 are equal due to the C_{3v} symmetry except for N_{Ga}^{3-} which is distorted due to the occupation of the $1e$ state.

Defect	d_1	d_2	d_3	d_4	ΔV(%)
N_{Ga}^{2+}	0.82		0.82		−44.0
N_{Ga}^{+}	1.28		0.79		−33.4
N_{Ga}	0.70		1.14		11.1
$V_{Ga}N_i$	1.54		0.81		−26.4
$V_{Ga}N_i^-$	1.49		0.95		7.1
$V_{Ga}N_i^{2-}$	1.45		1.01		24.4
$V_{Ga}N_i^{3-}$	1.55	1.27	1.27	0.77	45.1

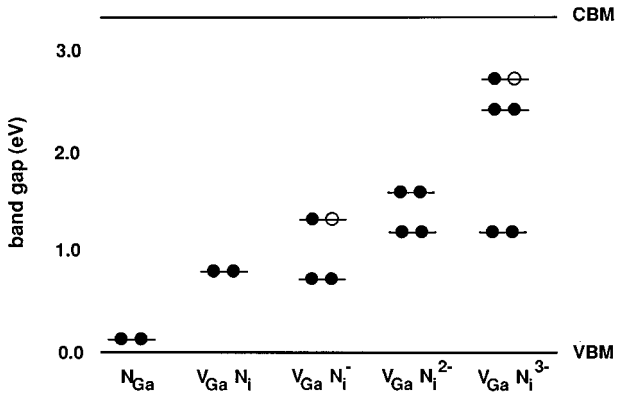

FIG. 2. The single particle energy levels (at the Γ point) in the band gap for different atomic positions and charge states of the nitrogen antisite. VBM and CBM refer to valence band maximum and conduction band minimum, respectively. Experimental value for the band gap is used.

The deep level character of the N_{Ga}^{2-} is illustrated in Fig. 3, where we plot the electron density associated with the uppermost doubly occupied $2a$ state. The localized character of the state is clearly visible and a large antibonding node is oriented along the [111] direction. The outward relaxation (see Table I) is due to the antibonding character of the $1a$ and $2a$ states and leads to a vacancylike open volume at the substitutional site. Similarly as in the case of the $EL2$ in GaAs, the experimental detection of such a defect could be carried out by the positron annihilation technique.[15]

The *positively* charged antisites do not exhibit the metastability observed for the neutral charge state when displaced in the [111] direction keeping all other atoms fixed. However, when all atoms are allowed to relax, N_{Ga}^{+} is characterized by a spontaneous move of the antisite atom in the [111] direction (for details see Table I). A similar behavior has been reported for substitutional N in diamond.[16] For the doubly positive antisite this phenomenon is removed and only a strong inward relaxation of the surrounding atoms is observed.

Given the unusual nature of the antisites, two important questions are whether N_{Ga} exists in appreciable concentrations in GaN, and which are the relevant charge states. The formation energies of N_{Ga} in different charge states as a function of the Fermi level position in the gap are presented

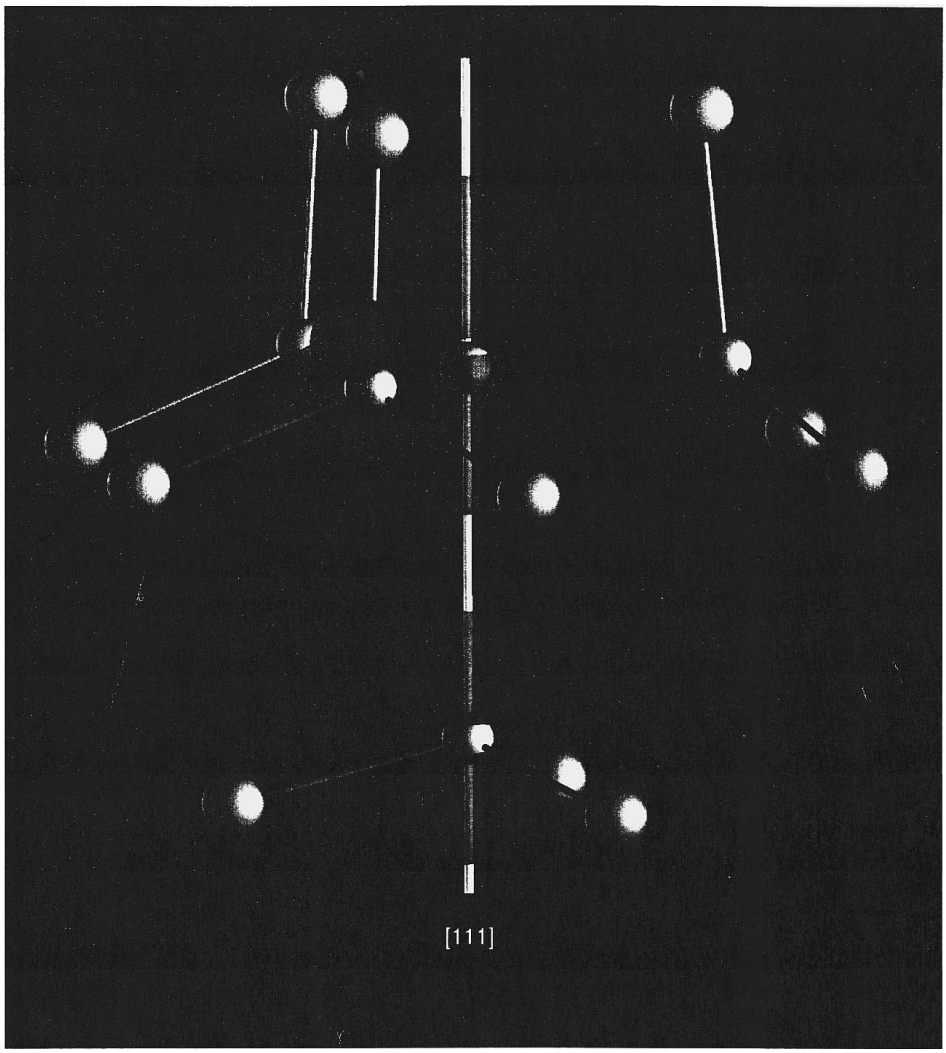

FIG. 3. The charge density for the highest occupied electronic state for N_{Ga}^{2-}. The blue (red) spheres denote nitrogen (gallium) atoms. The constant-value surface corresponds to the density $0.05e/\text{bohrs}^3$.

in Fig. 4 in nitrogen-rich conditions.[17] For *p*-type materials our calculations predict that the positive charge states should dominate. In *n*-type conditions, which are typical for undoped GaN, the negative charge states are the most favorable. The singly negative charge state is not stable at any Fermi level position; we predict that the N_{Ga} should be characterized by an ionization level where the charge state of the defect is changed by two electrons (negative-*U* behavior).

The total energy calculations by Neugebauer and Van de Walle[17] suggest that formation energies for antisites in GaN should be high, thus excluding their existence in large concentrations. Our calculations are in agreement with the work by Neugebauer and Van de Walle for the *neutral* N_{Ga}. However, Fig. 4 shows that the *negative* charge states at the *displaced* atomic configuration and at a high electron chemical potential are energetically several electron volts more favorable than the neutral defect, which leads to low formation energies in N-rich conditions. On the other hand, in Ga-rich conditions the formation energies for nitrogen antisites are several electron volts higher, which would prevent the existence of a large concentration of this defect type. Therefore we consider experimental confirmation for these defects to be essential before making definite conclusions. The deep levels observed by Götz *et al.*[18] show in this respect features which correlate with the deep levels found in our calculations.

A most interesting question is whether N_{Ga} is related to the parasitic yellow luminescence commonly observed in GaN samples. The yellow luminescence has a very wide spectrum and this is associated to strong phonon coupling.[19] The large atomic displacements for N_{Ga} in our calculations certainly indicate the presence of strong electron-lattice interaction, thus favoring the role of N_{Ga} as a candidate for the source of the yellow luminescence. Our calculations for hexagonal (wurtzite) GaN indicate that the negative nitrogen antisites have a similar tendency to be displaced along the threefold symmetry axis. The highest occupied levels descend considerably when the antisite atom is moved from the substitutional site to the displaced configuration. This could explain the contradictory result by Bogusławski, Briggs, and Bernholc[20] who propose that the highest electron level of a negatively charged antisite does not lie in the band gap. However, we find that the neutral antisite does not show the metastable behavior observed in the cubic phase. The calculations involving the wurtzite phase are essential because the experimental detection of the yellow luminescence has been

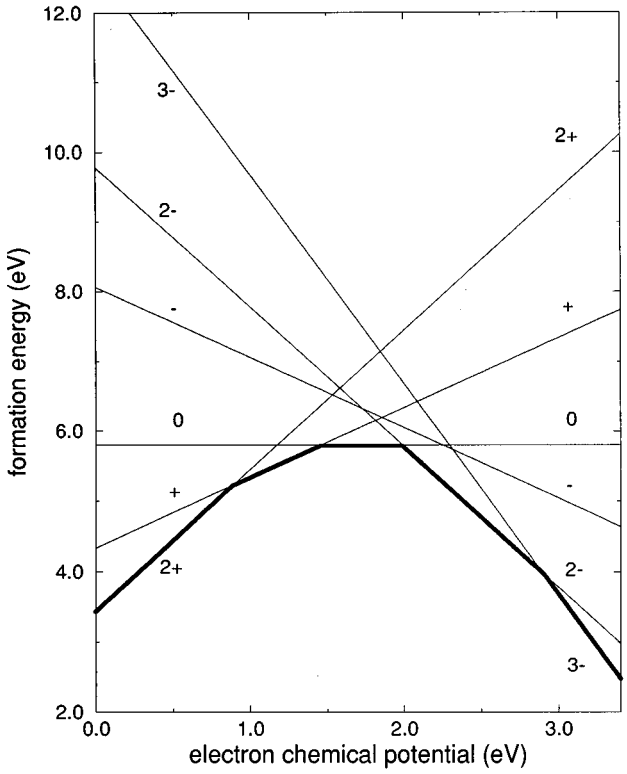

FIG. 4. The formation energies for N_{Ga} in different charge states as a function of the electron chemical potential in the band gap. The situation corresponds to the nitrogen-rich case and the experimental band gap value is used to give the limit for the electron chemical potential. Note that the formation energies correspond in all charge states to the displaced atomic configurations (except for N_{Ga}^{2+}). The ionization levels are characterized by negative-*U* behavior, which causes the singly negative charge state to be unstable.

performed mainly in hexagonal GaN.[19,21,22] Glaser *et al.*[21] suggest that the yellow luminescence is a deep-donor–shallow acceptor transition. A competitive view is offered by Suski *et al.*[22] who associate the yellow luminescence to a conduction-band/shallow-donor–deep-level transition, where their suggestion for the final state is the neutral N_{Ga}. We emphasize that our calculations predict that the nitrogen antisite induces several deep states, which can participate in both proposed transition models.

We have also performed tests for *c*-AlN and observe similar metastability for the neutral nitrogen antisite as in *c*-GaN. The negative nitrogen antisites are stable and distort into the [111] direction also in AlN due to the even larger band gap (6.2 eV) compared with GaN (3.4 eV). Another interesting aspect is related to the behavior of oxygen in these wide-band-gap materials. We suggest that the behavior of O at the cation site should resemble that of N_{Ga}^{-} in GaN due to the similar chemical identity of the atoms. Therefore, oxygen occupying a cation site, especially in the negative charge states, rivals the conventional model of O at an anion site.

In conclusion, our results for N_{Ga} shed new light on the origin of the deep levels in the band gap of GaN. The stability of several charge states is mediated by the large band gap, and similar phenomena are likely to exist in other wide-band-gap materials belonging to the III-V group. The observed large atomic displacements emphasize the role of electron-lattice coupling in GaN, and suggest a connection to the wide spectrum of the yellow luminescence.

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